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Invention: The Flameproof Finishing of Cellulose, Fibers and Articles Containing Them

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- ☐ Provisional Application
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SPECIFICATION

The Flameproof Finishing of Cellulose, Fibers and Articles Containing Them

7.6.1-11-02

Cross Reference to Related Applications

The present application claims priority under 35 U.S.C. §119 to German application 100 38 100.6, filed on August 4, 2000, the text of which is hereby incorporated by reference.

Field of the Invention

The invention is directed to a method for the permanent flameproof finishing of cellulose fibers by treating the fibers with a cyanuric chloride derivative in aqueous phase. The invention also includes the finished cellulose fibers and articles in which they are used such as yarns, fleeces and textile fabrics.

Background

Various methods are known which can be used for the permanent, *i.e.*, wash-resistant, and non-permanent finishing of cellulose fibers, especially cotton fibers. Flameproof textiles made using such finished fibers are used in proactive clothing, children's clothing, curtains and upholstery. Flameproof finishes often utilize inorganic salts such as ammonium hydrogen phosphate, ammonium sulfate, borax and boric acid, that can optionally be combined with organic nitrogenous bases. In particular, phosphorus flameproofing agents and phosphorus-nitrogen flameproofing agents are used for permanent flameproof finishing. These may be either adsorbed onto fibers or applied as a monomer or pre-condensate and hardened in the form of a polymer on the fiber. For example, pre-condensates of tetrakishydroxymethylphosphonium hydroxide and urea may be applied to the fiber, followed by a treatment with ammonia and then with hydrogen peroxide (*Melliand Textilberichte 3*:219-224 (1990)). This and similar methods are expensive and result in a product that is relatively stiff. A good flameproof finishing can also be achieved in the case of cotton using dialkylphosphono-carboxylic acid amides and melamine resins. However, this results in a substantial loss of tear strength.

Various ammino-1,3,5-triazines have also become known for their use in the permanent finishing of cotton and are bound via methylol groups to cellulose fibers. According to Schanz (*Textile Research Journal*, 418-422 (June 1977)) tetramethylol-2,4-diamino-6-(3,3,3-tribromo-1-propyl)-1,3,5-triazine functions as a flameproofing agent. This agent is applied in the form of an aqueous dimethylformamide solution and polymerizes at elevated temperature on the fiber. A significant disadvantage of this method, the use of dimethylformamide, is avoided in the method of Moreau *et al.* (*American Dyestuff Reporter*, 7-38 May (1970)) by using 2-amino-4,6-bis-diethoxy-phosphinyl-1,3,5-triazine or 2,4-diamino-6-diethoxy-phosphinyl-1,3,5-triazine in aqueous formaldehyde solution. Sello *et al.* (Textilveredelung 5:391-399 (1970)) teach other flameproofing agents based on 1,3,5-triazine compounds containing N-methylolamino- and phosphonic acid ester groupings. All these methods describe compounds that are bound to cellulose fibers by N-methylol groups. Aside from a loss of tear strength, the use of formaldehyde or a source of formaldehyde is a disadvantage.

It is known that cellulose can be reacted with cyanuric chloride or with 2-amino-4,6-dichloro-1,3,5-triazine in the presence of a base and that the reaction product can be subsequently reacted with a dye (U.S. 1,886,480; U.S. 2,025,660; Rauh, *Melliand Textilberichte 10*:1195 – 1200 (1971)). However, these references do not suggest that cotton can be flameproofed by reaction with dichlorotriazinyl amines or similar compounds. Dichlorotriazinyl amino compounds containing sulfonic acid groups (see *e.g.*, WO 97/49856) as well as quaternary compounds based on bistriazinyl amines with one chlorine atom each in the triazine ring (see *e.g.*, Evans, *JSDC 100*:304-314 (October 1984)) can be used as auxiliary textile agents for modifying cellulose in order to improve its dyeing affinity.

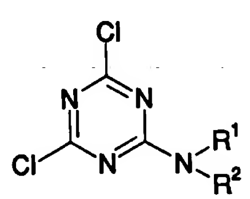
An important prerequisite for the successful use of reactive triazine derivatives in flameproof finishing, is to achieve a high degree of substitution during the reaction of the triazine derivative with the cellulosic material. With respect to the dyeing qualities of the material, experience has shown that an even slight modification of the cellulose material

with the triazine derivatives cited has a great influence. However, in order to achieve a flameproofing effect or self-extinguishing qualities, it is necessary to apply a large amount of compound and this tends to make procedures expensive.

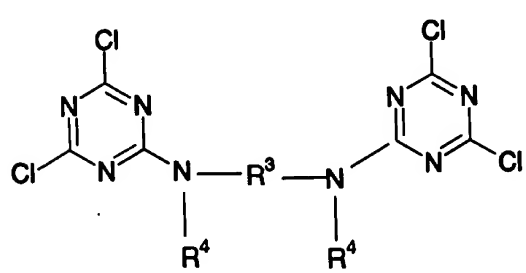
Ideally a method for flameproof finishing should allow a high degree of substitution of cellulosic material under economically acceptable conditions and avoid the use of formaldehyde or substances that release formaldehyde. In addition, it should feasible to carry out the method with the customary devices of a textile operation and, in particular, the high expense for an ammonia vaporization plant should be avoided. Finally, the method should make it possible to achieve the permanent flameproofing or self-extinguishing of cellulose fibers with an LOI value (limiting oxygen index according to ASTM D2863-77) of 24 or 27 and higher without appreciably influencing the tear strength.

Summary of the Invention

The present invention is concerned with a method for flameproof finishing that does not have the disadvantages of the previously known methods. It involves exposing cellulose fibers or the articles containing them to alkaline conditions to swell fibers, and then treating them with a cyanuric chloride derivative in aqueous-alkaline phase. The cyanic chloride derivative is a 4,6-dichloro-1,3,5-triazine-2-yl amine of formula I or II:



(I)

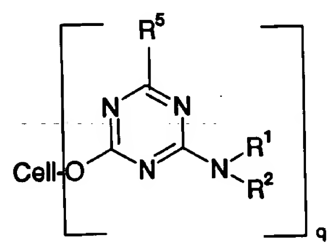


(II),

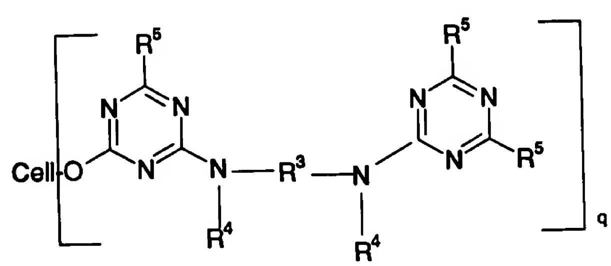
in which R^1 and R^2 are the same or different and are selected from the group consisting of: H; $(C_1 - C_6)$ alkyl; benzyl; phenyl; ω-amino $(C_2 - C_6)$ alkyl; ω-hydroxy $(C_2 - C_6)$ alkyl; $(CH_2)_mSO_2$-OH or $-(CH_2)_m$-COOH, in which m is 1 or 2, as well as their amides; $(CH_2)_n$-P(O)(OR')$_2$ in which n = 1, 2 or 3 and R'= H, CH_3 or C_2H_5; o-, m- or p-$C_6H_4SO_2NH_2$; and o-, m- or p-C_6H_4-$N(CH_3)_3^{\oplus}$; or R^1 and R^2 together form an ethylene trimethylene- or bismethylene imino group; R^3 in formula II is selected from the group consisting of: para- or meta-phenylene; 1,4-, 1,3- or 2,6-naphthylene; $(C_2 - C_6)$ alkylene; -C_2H_4-NH-C_2H_4-; C_2H_4-NH-C_2H_4-NH-C_2H_4-; C_2H_4-O-C_2H_4-; and C_6H_4-NHCONH-C_6H_4- ; and R^4 is selected from the group consisting of: H; $(C_1 - C_3)$ alkyl; aminoethyl; and aminopropyl; or both R^4 groups together form ethylene or propylene.

The method in accordance with the invention achieves permanent flameproof finishing of cellulose fibers and articles containing them such as yarns, fleeces and sheet articles, e.g., fabric, knit goods and knitwear. The finished fibers contain amino-s-triazine compounds bound to glucose units of the cellulose via ether bridges. The permanently finished cellulose comprises a structure in accordance with formula III or IV:

In formulas III and IV the groups R^1, R^2, R^3 and R^4 have the same definitions as for formulas I and II; R^5 stands for Cl, OH, Ocell, OR^6 or NHR^6, with R^6 standing for a



(III)



(IV),

dye group; "cell" stands for an anhydroglucose unit of cellulose and q for the degree of substitution. Q can assume any value in the range of greater than 0 to 3. Although, in the first stage of the method, R^5 is still generally chlorine, it can be converted by further reaction with a glucose unit of cellulose into Ocell or by a reaction with a dye into OR^6 or NHR^6.

A permanent flameproof finishing results from the chemical reaction of the derivative with cellulose. This type of finishing may be contrasted with previous flameproof finishings in which polymers are embedded in the fiber and cross-linked. In the present method, covalent linkage of the active substances to the fiber creates no appreciable loss in tear strength or in the gripping qualities of sheet materials.

The concept "flameproof finishing" is to be understood to mean that the finished cellulose fiber and articles containing it are less readily combustible and/or extinguish themselves more rapidly after the removal of the source of ignition than is the case for non-finished fiber or articles containing it. A measure for flameproof finishing is the so-called LOI value according to ASTM D2863-77. The LOI indicates the limit value of the volumetric fraction of oxygen in an oxygen/nitrogen atmosphere in which a textile fabric is still burning from the top downward. The higher the LOI value the better the flameproof finishing. Above a LOI of 24 one speaks of flame-retarding qualities and at values of 27 and higher of self-extinguishing qualities.

The quality of the flameproof finishing is a function of the components with active flameproofing and amount used relative to the fiber weight. As is apparent from the state of the art nitrogenous compounds and phosphorous-containing compounds act in a flameproofing manner. The cyanuric chloride derivatives used in accordance with the invention make it possible to adjust the nitrogen content of the cellulose to values that bring about a flameproofing or self-extinguishing quality. Self-extinguishing qualities are to be expected, *e.g.*, in cotton fibers or a cotton article at an N content of approximately 3 %. Self-extinguishing qualities can be expected at a P content of approximately 2.2 % when using a phosphorus-containing flameproofing agent. The two elements can be

substituted; a synergistic effect is frequently achieved by the combination of both elements.

The cyanuric chloride derivatives in accordance with the invention are reactively linked with the OH groups of the cellulose. Theoretically, three hydroxyl groups per anhydroglucose unit are available for reaction, so that a maximum value of 3 for the degree of substitution results. This high degree of substitution is possible in the case of cellulose either only in a homogeneous reaction or, in the case of a heterogeneous reaction, only if cellulose fibers have been pre-swollen. Moreover, complete substitution can usually only be achieved for a very few, usually non-polar, substituents (e.g., trimethylcellulose, trimethylsilylcellulose). In the case of sterically exacting substituents, such as triazine derivatives, and that are applied in aqueous solution, usually far lesser degrees of substitution are obtained, even under drastic reaction conditions. Thus, it can be calculated, e.g., that given a coloration of average depth with reactive dyes (e.g., dichloro- or monochloro- reactive anchor dye) a substitution takes place only on every twentieth to fiftieth anhydroglucose unit.

In order to obtain higher degrees of substitution, which are a prerequisite for a flameproof finishing (see nitrogen content), the cyanuric chloride derivatives used in accordance with the invention are applied after a preceding swelling of the fibrous material in aqueous alkali. According to a preferred embodiment, at least 0.05 mole cyanuric chloride derivative according to formula I or at least 0.025 mole of the derivative according to formula II is used per glucose unit of the cellulose. The cyanuric chloride derivative is preferably used in an amount such that the degree of substitution, q, is in the range of approximately 0.1 to 1. Depending on the structure of the cyanuric chloride derivative, a different nitrogen content of the finished cellulose will result. The dichlorotriazinyl derivative according to formula I or II is advantageously used in such an amount that the finished cellulose has a nitrogen content of at least 2 % by wt., and preferably 3 to 10 % by wt. Cyanuric chloride derivatives in accordance with the invention are advantageously used in an amount of 10 to 100 % by wt., and preferably 20 to 80 % by wt.

Figure 1 shows the dependency of the LOI value on the nitrogen content of the cotton article that has undergone flameproof finishing. The finishing took place using 2-ammino-4,6-dichlorotriazine. The figure includes measurements derived from examples 1 and 2.

It is possible to treat cellulose fibers with a phosphorus-containing flameproofing agent before, during, or after finishing in accordance with the invention. Such treatment will result in the phosphorus-containing flameproofing agent encasing the cellulose fibers in the form of a polycondensate or, preferably, the phosphorus-containing agent will react with the fibers. The phosphorus-containing , or other, flameproofing agent is used in an amount such that the finished cellulose has a phosphorus content of at least 1 % by wt., and preferably at least 2 % by wt.

The cellulose fibers that are to be permanently finished can be native fibers, especially cotton fibers, solvent-spun cellulose fibers such as, e.g., lyocell, or regenerated fibers such as viscose fibers or carbamate fibers. The cellulose fibers can be used in the form of a flock, fleece, fabric, knit goods or knitwear or other sheet article. Yarns consisting essentially of cellulose fibers can also be used. Yarns and sheet articles that also contain fibers other than cellulose should generally only be used in the method, if the other fibers can enter into a chemical bond with the cyanuric chloride derivative in a manner similar to that of a cellulose fiber. Naturally, cellulose fibers finished in accordance with the invention can be combined with other fibers that are, optionally, flameproof finished in a completely different manner, and converted into yarn and textile articles.

In order to carry out the method of the invention, the cellulose fiber or an article containing it is customarily reacted in aqueous, alkaline phase with the cyanuric chloride derivative. When cotton or cotton articles are used, the treatment can advantageously be carried out in such a manner that at first a treatment with sodium hydroxide solution takes place, during which the cotton swells. After being squeezed to a residual moisture of below 100% the cellulose alkalized in this manner is brought in contact with an aqueous

solution or a suspension of a cyanuric chloride derivative of formula I or II. This contacting can take place in the presence or the absence of customary textile agents such dispersing agents. The treatment can be carried out in apparatuses familiar to those skilled in the art of textile treatments, *e.g.*, in a dyeing apparatus. Treatment can be carried out at room temperature, but, preferably, a moderately elevated temperature is used, preferably in the range of 30 to 80°C, and more at 50 to 70°C. Treatment time may vary from a few minutes to a few hours.

The required amount of cyanuric chloride derivative can be applied onto the fiber in one step or in several steps. After the actual treatment, non-reactively bound cyanuric chloride derivative and excess alkali are washed away with water, preferably boiling water. During this post-treatment, chlorine atoms still present on the cyanuric chloride are replaced by hydroxyl groups. After the treatment of the cellulose fiber with the cyanuric chloride derivative, the resulting product may be dyed with a customary dye for cellulose before or after post-treatment. In so far as the finished cellulose still has reactive chlorine atoms on the cyanuric chloride before the dyeing process, the dye can be reactively bound to them. As an alternative, the flameproof finishing of the invention can also be carried out on a cellulose fiber that is entirely or partially dyed or on an article containing it.

The treatment of cellulose with a cyanuric chloride derivative, as well as its post-treatment or fixing are customary process steps in the textile art. Procedures and techniques that are apparent from the existing art are part of the invention.

Among the cyanuric chloride derivatives that are to be used in accordance with the invention and that are a dichlorotriazinyl amines according to formula I or bis(dichlorotriazinyl)diamines according to formula II, the following compounds are especially preferred: 2-amino-4,6-dichlorotriazine; 2-aminoethylamino-2,4-dichloro-triazine; 2-(p-benzenesulfonamide-amino)-4,6-dichlorotriazine; a salt, especially a halogenide of 2-(p-trimethylammonium-benzene-amino)-4,6-dichlorotriazine; bis-N,N'-4,6-dichloro-triazine-2-yl)-p-phenylene diamine; bis-N,N'- 4,6-dichlorotriazine-2-yl)-(C_2 to C_4) alkene diamine; and bis-(4,6-dichlorotriazine-2-yl)-aminoethylphosphonate.

If a phosphorus-containing agent is used for flameproof finishing in addition to a cyanuric chloride derivative as described above, this can take the form of a single agent, i.e., a phosphorus-containing triazine derivative in accordance with the invention. However, it is also possible to apply a phosphorus-containing flameproofing agent onto the fiber by further treatment, *e.g.*, by treating the fiber with a flameproofing agent selected from dialkylphosphonocarboxylic acid amides and their methylol compounds, phosphonates and/or tetrakishydroxymethylphosphonium salts.

Preferred cellulose fibers produced in accordance with the invention or articles containing them comprise the groups R^1, R^2, R^3 and R^4 in the structural elements according to formula III or IV. R^5 preferably stands for OH and/or Ocell. A cross-linking of the cellulose can occur to a certain extent by using the dichlorotriazinyl compounds or bis(dichlorotriazinyl) compounds of the invention. A crease-resistant finish is achieved at the same time as the flameproof finish as a result of this cross linking. In a manner similar to that described for the flameproof finishing, the creaseproof finishing is a function of the amount and reactivity of the dichlorotriazine compound used and, in addition, of conditions such as temperature, pH and concentration used during treatment and the post-treatment.

Advantages of the method include the ability to carry out treatment in a simple manner, the ready accessibility of the cyanuric chloride derivatives suitable for use as flameproofing agents and their high content of the nitrogen necessary for flameproofing. The degree of flameproofing can be adjusted based upon the amount of cyanuric chloride derivative used and, in addition, based upon the use phosphorus-containing flameproofing agents. A LOI value of above 25 can be easily achieved. Another advantage is that tear strength is only minimally reduced while, at the same time, crease resistance increases. The use of a cationic cyanuric chloride derivative makes it possible to obtain a higher degree of exhaustion in subsequent dying steps. Thus, more intensive dying can be achieved.

The following non-limiting examples illustrate the invention.

Examples

Example 1:

A cotton fabric strip (16 g, scoured, bleached, 136 g/m^2) is swollen for 3 min. in 700 ml sodium hydroxide solution (300 g/l). The material is subsequently squeezed out to a residual moisture of 80%. The strip is placed loosely wound into a bucket of high-grade steel and compounded with a suspension of aminodichlorotriazine (4 g, 165 g/mol, 0.024 mol) in 50 ml water containing 0.2 g of a dispersing agent (naphthalene sulfonate). It is heated in a laboratory dyeing apparatus (Polymat of the Ahiba company in Switzerland) to 65°C and agitated 1 hour at this temperature. Non-reacted aminodichlorotriazine and excess sodium hydroxide solution are then washed out with boiling water.

A nitrogen content of 3% is obtained. The LOI of the finished fabric is 21.6, which may be contrasted with that of the untreated cotton fabric, 17. The tear strength, determined using a test according to DIN 53859 is 7.3 N (F_{agent}) for the untreated fabric and 7.2 N for the fabric finished with aminodichlorotriazine. Thus, it decreases only to a negligible extent. The angle of wet crease recovery increases by the treatment from 66° to 110° (complete recovery 180°).

Example 2:

A cotton fabric strip (16 g, scoured, bleached, 136 g/m^2) is swollen for 3 min. in 700 ml sodium hydroxide solution (300 g/l). The material is subsequently squeezed out to a residual moisture of 80%. The strip is impregnated with a suspension of aminodichlorotriazine (4 g, 165 g/mol, 0.024 mol) in 50 ml water containing 0.2 g of a dispersing agent (naphthalene sulfonate). The strip is subsequently wound on a roller, packed airtight and agitated for 24 hours (cold pad-batch dyeing process). Then, non-reacted aminodichlorotriazine and excess sodium hydroxide solution are washed out with boiling water.

A nitrogen content of 1.6% is obtained. The LOI of the fabric is 19.1.

Example 3:

A cotton fabric strip (16 g, scoured, bleached, 136 g/m^2) is swollen for 3 min. in 700 ml sodium hydroxide solution (300 g/l). The material is subsequently squeezed out to a residual moisture of 80%. 2-(p-benzene sulfonamide-amino)-4,6-dichlorotriazine (8 g) is dissolved under addition of sodium carbonate in 50 ml water. The caustified cotton strip is placed with this solution into a high-grade steel bucket. The preparation is heated in a laboratory dyeing apparatus to 65°C and agitated one hour at this temperature. Then, non-reacted 2-(p-benzene sulfonamide-amino)-4,6-dichlorotriazine and excess sodium hydroxide solution are washed out with boiling water.

A nitrogen content of 2.4% is obtained. The LOI of the fabric is 22.

Example 4:

A cotton fabric strip (16 g, scoured, bleached, 136 g/m^2) is swollen for 3 min. in 700 ml sodium hydroxide solution (300 g/l). The material is subsequently squeezed out to a residual moisture of 80%. Bis-N,N′-(4,6-dichloro-2-amino-triazinyl)-p-phenylene diamine (4 g, 404 g/mol, 0.01 mol) is suspended in 50 ml water with the addition of 0.2 g of a dispersing agent (Avolan IS). The caustified cotton strip is compounded with this solution in a high-grade steel bucket. The preparation is heated to 65°C in a laboratory dyeing apparatus and agitated one hour at this temperature. Then, non-reacted bis-N,N`-(4,6-dichloro-2-amino-triazinyl)-p-phenylene diamine and excess sodium hydroxide solution are washed out with boiling water.

A nitrogen content of 4.6% is obtained. The LOI of the fabric is 23.

Example 5:

A cotton fabric strip (16 g, scoured, bleached, 136 g/m^2) is swollen for 3 min. in 700 ml sodium hydroxide solution (300 g/l). The material is subsequently wrung out to a residual moisture of 80%. 2,4-dichloro-6-(m-trimethylammonium-benzeneamino)-triazine iodide (8 g, 426 g/mol, 0.019 mol) is dissolved in 50 ml water. The caustified cotton strip is compounded with this solution in a high-grade steel bucket. The matter is heated to

65°C in the laboratory dyeing apparatus and agitated for one hour at this temperature. Non-reacted 2,4-dichloro-6-(m-trimethylammonium-benzeneamino)-triazine iodide and excess sodium hydroxide solution are then washed out with boiling water.

A nitrogen content of 1.3% is obtained. The LOI of the fabric is 18.5.

Example 6:

A cotton fabric strip treated with aminodichlorotriazine (8 g, nitrogen content 2.2 %) is impregnated with a solution of 13 g sodium dihydrogen phosphate in 100 ml water. It is wrung out to a residual moisture of 80% and the fabric strip dried at 60°C.

An additional coating weight of 9.8% is obtained. The LOI of the fabric rises from 20 to 27.2.

Example 7

A cotton fabric strip treated with aminodichlorotriazine (8 g, nitrogen content 3 %) is impregnated with a mixture of 60 g of a dialkylphosphono carboxylic acid amide solution (Aflammit KWB, Thor-Chemie), 3.5 g phosphoric acid and 40 ml water. The strip is wrung out to a residual moisture of 80% and dried 1 min. at 100°C in a laboratory dryer (Mathis AG, Switzerland). The strip is then fixed in the same device at 150°C for 5 min. The fabric strip is washed hot and then several times cold.

A phosphorus content of 2.5 % and a LOI of 32 is obtained. The wash resistance of the finish is just as good as in the case of an untreated fabric in which the finishing bath contains a cross-linking agent.

Example 8

A cotton fabric strip treated with aminodichlorotriazine (8 g, nitrogen content 3%) is impregnated with a solution of 16 g ammonium monomethylphosphite and 8 g urea in 24 ml water. The strip is wrung out to a residual moisture of 80% and dried 1 min. in a

laboratory dryer at 100°C. The strip is then fixed in the same device at 150°C for 5 min. The fabric strip is washed hot and cold.

A phosphorus content of 3% and a LOI of 38 is obtained. The finishing lasts through five 60°C washes.

Example 9

A cotton fabric strip treated with aminodichlorotriazine (1.8 g, nitrogen content 2.2%) is dyed with a cationic dye (Basic Blue 4; 4% dyeing at a liquor ratio of 1:50) with the addition of 1.35 ml 60% acetic acid, 1.8 g sodium acetate and 9 g sodium sulfate at 85°C for 45 min. The strip is then washed several times.

The degree of exhaustion of the dyeing rises from 30 % (untreated fabric) to 41 % (fabric pretreated with AdCT). Distinctly more dye is also fixed on the fabric; the K/S value rises from 2.1 to 11.2.

Example 10

A cotton fabric strip treated with 2,4-dichloro-6-(m-trimethylammonium-benzeneamino)-triazine iodide (1.8 g, nitrogen content 1.7%) is dyed with a reactive dye (Reactive Black 5; 5% dyeing at a liquor ratio of 1:20) with the addition of 50 g/l sodium sulfate, 15 g/l sodium carbonate and 1.5 ml/l sodium hydroxide solution (32.5 %) at 60°C for 1 hour. The strip is then washed hot and cold several times.

The degree of exhaustion of the dyeing rises from 58% (untreated fabric) to 65% (pretreated fabric). Distinctly more dye is fixed on the fabric; the K/S value rises from 23 to 26.1.